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A FIVE-TO-TENFOLD IMPROVEMENT IN DOSE RESISTANCE OVER EPOXIES

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MECHANICAL STRENGTH OF LOW-TEMPERATURE-IRRADIATED POLYIMIDES: A FIVE-TO-TENFOLD IMPROVEMENT IN DOSE-RESISTANCE OVER EPOXIES

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Neutronics calculations by Engholm [1] show that without additional shielding even the first fusion test reactors such as the Fusion Engineering Device will produce lifetime doses at magnet insulator locations that exceed the radiation tolerance of glass-fabric-filled (gff) epoxies now used. To explore the possible use of an alternative insulator, the mechanical strength of pure and recently available gff polyimides was studied as a function of gamma-ray irradiation at 4.9 K to 100 MGy (10^{10} rads). After a postirradiation anneal at 307 K the flexure and compressive strengths of the gff materials measured at 77 K were reduced by up to 40% for 100 MGy while the pure material changed little. Testing done at 300 K gave similar results, but all stress values were about 40% less. Compared to earlier epoxy studies [2] we find that, overall, the gff polyimides are 5 to 10 times more radiation resistant than comparably prepared gff epoxies.

1. INTRODUCTION

A program is under way at ORNL to study the irradiation behavior of organic insulating material that may be used in the construction of large superconducting coils that provide magnetic containment for the plasma in a fusion reactor. The use of such materials provides an economical method for producing not only electrical insulation but also mechanical support needed in coil construction. Although many studies on the effects of radiation on organic insulators exist, there are few on the most recently developed materials or on the simultaneous effects of radiation and low temperatures. Recent calculations by Engholm [1] show that without additional protective shielding even the first test reactors such as the Fusion Engineering Device (FED) will produce liftime doses at magnet insulator locations that exceed the radiation tolerance of glass-fabric-filled (gff) epoxies in present use.

The superior radiation resistance of pure polyimide, Vespel, at room temperature has been known for some years; however, it does not have sufficient strength for the application. Only recently have gff polyimide materials become available which have a strength in the unirradiated condition comparable to gff epoxies and sufficient to meet design needs. For these reasons a study of the mechanical properties of pure and gff polyimides was made on specimens irradiated at 4.9 K to various gamma-ray doses up to 100 MGy (10^{10} rads). In the service conditions it is, of course, necessary that the electrical properties of magnet insulators also maintain design standards throughout the lifetime of the magnet. Previous studies [2] of polyimide material irradiated under the same conditions and to the same dose found no significant change in either electrical resistance or breakdown voltage.

Tests in this program were made after irradiation at 4.9 K and warmup to room temperature. This is a meaningful procedure, since it is expected that over their lifetime fusion-reactor magnets occasionally will be warmed to 300 K. Our knowledge of the strength of insulators under cyclic conditions is just as essential as that under static cold conditions. Since the cost of testing at liquid-He temperature after irradiation without warmup is many times greater than with warmup, tests of the first type were excluded in an effort to maximize the information we could obtain with available funds. Tests without warmup after irradiation on candidate materials selected from present studies are essential in future work. Takamura and Kato recently studied the pure polyimide, Vespel, and various preparations of one epoxy, Epon 828, after reactor irradiation at 5 K to 11 MGy (1.1 × 10^9 rads).[3] They made postirradiation tests at 4.2 and 77 K without prior warmup. In the case of Vespel they observed virtually no change in compressive strength at 77 K in agreement with the results presented in this report, which were obtained with prior warmup. A further comparison with our earlier epoxy study [2] is difficult to make because of the dissimilarity in material preparation. In general, however, there is qualitative agreement between the two studies for filled Epon 828.

2. MATERIALS

Gff materials were especially prepared by cooperating manufacturers, while the unfilled polyimide, Vespel, is available commercially. The following list gives the material designation as used in this report and a brief description

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of each. For a description of the gff epoxies to which the present results are compared, see Ref. [2].

1. Vespel -- (SP-1) unfilled polyimide; E. I. DuPont de Nemours and Company.

2. Spauldite -- SPAULDITE® SPAULRAD™; Spaulding Fibre Company; a high-pressure laminate composed of aromatic polyimide resin reinforced with continuous filament E glass-woven fabric 70-71% by weight.

3. Kerimid -- Kerimid® 601 laminate; Norplex Division, VOP, Inc.; a balanced resin of bismaleimide and aromatic diamines reinforced with E glass-woven fabric 40-60% by weight.

3. EXPERIMENTAL DETAILS

3.1 Types of Tests and Sample Specifications

Specimens for testing flexure and compressive strengths were divided into two identical groups, one for irradiation and the other for unirradiated controls. Flexure tests were made at 300 and 77 K, while compression tests were made only at 77 K. Compression tests of Spauldite were only in the direction parallel to the glass fiber laminations, while tests of Kerimid were parallel and perpendicular to the laminations. Three tests were made for each condition of material, temperature and orientation, making a total of 30 control and 30 irradiated specimens. Flexure tests at 77 K on Spauldite and Kerimid were made in 3-point bending, while all others were made in 4-point bending with 25 mm between supports for both cases. Fracture stress and linear flexure modulus were calculated using formulations in the ANSI/ASTM D 790-71(78) code. Dimensions of the specimens in mm were 1.6 x 3.2 x 50 for the flexure sticks and 6.4 d x 12.7 ℓ for the compression rods.

3.2 Irradiation Conditions

As in previous experiments [2] the specimens were contained in a basket made of Al screen which was surrounded by a 0.13-mm-thick Cd shield. This capsule was then inserted into the sample chamber of the ORNL Low Temperature Irradiation Facility (LTIF) located at the Bulk Shielding Reactor. The Cd shield converted 92% of the impinging thermal-neutron flux present in the LTIF into gamma rays via an (n,γ) reaction. The combination of Cd shield and ambient gamma rays gave an intensity of 0.53 MGy (5.3 x 10^7 rads) per hour with energies mostly in the range 0.5 to 5 MeV.

The conditions during irradiation in liquid He at 4.9 K were identical to those in previous studies of epoxies.[2] It was shown then that the small fast-neutron fluence (3.7 x 10^{20} n/m^2 > 0.1 MeV) accompanying the 100-MGy (10^{10} rads) γ-ray dose had no detectable effect upon the mechanical strength of gff epoxies. We expect the same result would be true in this experiment for the gff polyimides. This is not to say that fast neutrons are unimportant. In many fusion reactor magnet locations, fast-neutron fluences will greatly exceed those we have studied. The response of the strength of polyimides to fast-neutron fluence remains as an important matter for new study.

As in earlier irradiations, the major sources of damage were gamma rays and energetic fission fragments. The latter are produced only in the gff materials as a result of the fission of ^{10}B atoms (present as B_2O_3 in the glass) by capture of thermal neutrons that penetrate the Cd shield. In our earlier report[2] we incorrectly stated the glass content in the gff epoxies as 33.7 wt %. We now know by reconfirmation from the manufacturers that the glass content was 66.3 wt %, and hence the energy deposition rate from ^{10}B fission was 1.25 times that due to gamma rays, and not 0.64 as was stated. In the present experiment the glass content of the Spauldite was 70 wt %, which is very close to that in the previously studied epoxies. In the case of Kerimid a value between 40-60% is given by the manufacturer, and, of course, Vespel has no glass. All doses in this report are given only in terms of energy deposition by gamma rays, which is common to all the materials. It is important to note that while we calculate the additional dose received by each material from ^{10}B fission (for details see Ref. [2]), there are insufficient data to determine if energy deposition is a valid criterion for predicting property changes which are produced by radiations having different damage-production mechanisms such as gamma rays and ^{10}B fission fragments. The calculations gave the following results:

Material	Dose Ratio ^{10}B fission/gamma ray
Vespel	0
Spauldite	1.33
Kerimid	0.95

Values for the highest dose to the samples were:

Gamma-ray dose	100 MGy (10^{10} rads)
Thermal-neutron fluence	3.1x10^{21} n/m^2
Fast-neutron fluence	3.7x10^{20} n/m^2 > 0.1 Mev
Irradiation time	189 hrs

Values for smaller doses are reduced proportionately.

4. *RESULTS OF MECHANICAL STRENGTH TESTS*

The results of all mechanical strength tests of the polyimides studied in this experiment are shown in Fig. 1. For comparison the results for similarly prepared epoxy materials irradiated under the same conditions are shown in Fig. 2.

4.1 Flexure Fracture Stress

Several distinguishing features are noted for the flexure-strength results:

1. In the unirradiated condition the gff Kerimid and Spauldite are, respectively, 2.2 and 3.1 times stronger at 77 K than the unfilled Vespel, and the best, Spauldite, has 90% of the strength of the gff epoxies.

2. At 100 MGy (10^{10} rads) Vespel loses only 8%, Kerimid 30%, and Spauldite 38% of initial strength at 77 K, but the latter remains about 25 - 40% stronger than Kerimid throughout the entire dose range, possibly because of the greater glass content in Spauldite.

3. At a dose of 24 MGy (2.4×10^9 rads) the better gff polyimide (Spauldite) is about five times stronger than the best gff epoxy (G-11 CR) for tests at 77 K. At this dose the epoxy probably has insufficient strength for practical use while, in contrast, the polyimide remains usable to a dose 4 times as large.

4. The well-known temperature dependence of the strength of polyimides (increasing strength with decreasing temperature) was observed in both unirradiated and irradiated specimens.

4.2 Linear Flexure Modulus (LFM)

With increasing dose the LFM at 77 and 300 K slightly increased for Vespel and decreased for the others. The initial and 100-MGy (10^{10} rads) values (G Pa) were:

	77 K	300 K
Vespel	7.5 — 9.6	4.3 — 5.1
Spauldite	29 — 28	28 — 24
Kerimid	27 — 24	26 — 22

4.3 Compressive Strength

In the case of compression tests, all of which were made at 77 K, Kerimid material was available to prepare specimens that could be loaded perpendicular (Kerimid ⊥) as well as parallel (Kerimid ||) to the glass-fabric laminations, while Spauldite was tested only with loading parallel to the laminations. The results shown in Fig. 1 have some notable features:

1. In the unirradiated condition the Spauldite and Kerimid || show a much smaller difference in strength compared to the difference seen for flexure strength at 77 K, and the Kerimid ⊥ is about 40% stronger than Kerimid ||.

2. Spauldite shows a nearly linear decrease in strength with dose compared to the slightly concave-up response of Kerimid ||. Although the responses follow different paths the two materials reach nearly the same strength at 100 MGy (10^{10} rads) -- down about 45% from initial unirradiated values.

3. The unfilled polyimid, Vespel, shows a slight linear increase in strength with dose reaching 8% at 100 MGy (10^{10} rads).

4. In the case of Kerimid ⊥ no loss in strength was observed for 100 MGy (10^{10} rads). Within the scatter of the data a constant-strength line might represent the behavior nearly as well as the indicated concave-up curve which connects average values. Since present reactor designs show some material stressed perpendicular to the laminations, further study to doses greater than 100 MGy (10^{10} rads) to determine the radiation tolerance for this orientation could give useful results.

5. RADIOACTIVITY

The thermal-neutron-produced radioactivity of the materials measured as in [2] was found to decrease by a factor of 2.5 between one and four weeks after the irradiation to 100 MGy (10^{10} rads). By comparing the results for the unfilled Vespel with Spauldite and Kerimid, it was clear that almost all of the radioactivity originates in the glass. Further, the gff polyimides gave almost the same results as G-10CR, which has nearly the same glass content.

6. GAS EVOLUTION

At the end of each of two successive intervals after irradiation the gas mixture evolved by all samples was completely removed and analyzed as in [2]. It can be noted in Table I that the composition changes markedly with time after irradiation. The first sample shows a much larger proportion of H_2 indicating its more rapid diffusion out of the material compared to the heavier species.

Table I

Gases Evolved at 307 K After Irradiation at 4.9 K to 100 MGy (10^{10} rads) (10^{-4} grams gas/gram resin)

	Interval After Irradiation (Days)	
	0-1	1-5
H_2	14.3	0.2
CH_4	0.3	0.5
H_2O	0.6	7.4
N_2 and CO	16.0	23.4
O_2	0.02	0.1
CO_2	0.9	3.2
C_2H_4	0.2	0.4
Total	32.3	35.2

If polyimides find use in vacuum and/or coolant systems of a fusion reactor magnet, then consideration should be given for methods to purge the systems of contaminants shown in Table I which would evolve during periodic warm-ups of the magnet system.

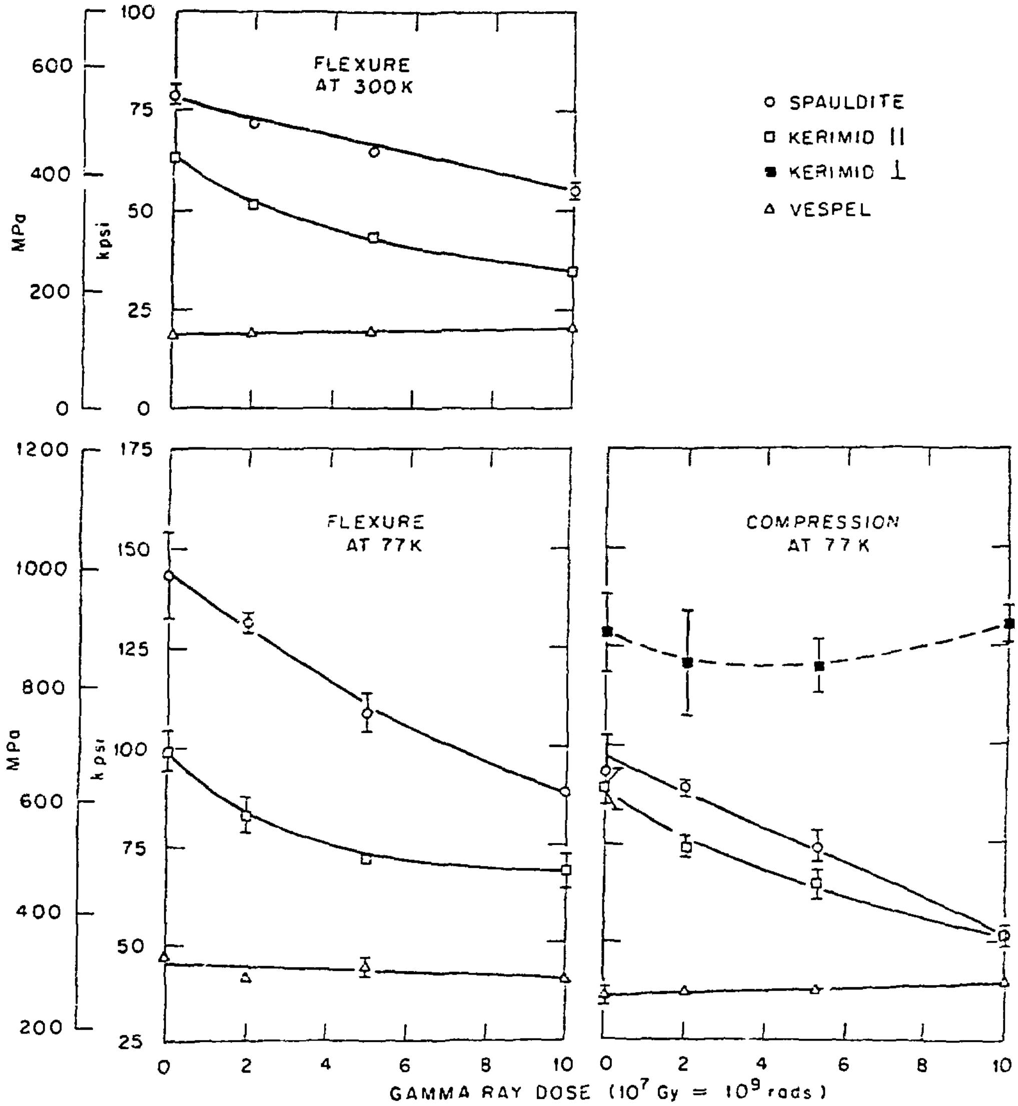

Figure 1: Results of fracture strength tests on pure and glass-fabric-filled (gff) polyimides after irradiation at 4.9 K followed by warmup to 307 K. Each data point shows the average value of three tests, and error bars indicate avg. dev. Points without error bars indicate data scatter was too small to show. See text for accompanying ^{10}B fission dose.

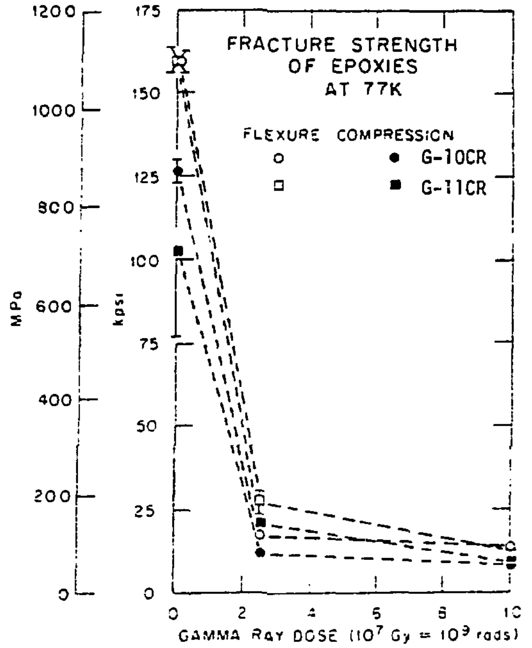

Figure 2 : The effect of irradiation on gff epoxies obtained as in Fig. 1. The dashed lines serve only as a guide for connecting related data points and are not intended to give intermediate strength values.

7. CONCLUSIONS

1. The gff polyimide data in Fig. 1 indicate the loss in strength with dose reaches an average of ∿ 35% at 100 MGy (10^{10} rads). In comparison Fig. 2 shows no data for the gff epoxies in the corresponding responsive range of loss of strength. *To make an approximate* comparison between the two materials we assumed no loss in epoxy strength up to 2 MGy (see results for G-10 [4]) and a linear decrease thereafter to the values indicated at 24 MGy. We then compared radiation doses for 30% and 40% losses in both flexure and compressive strength at 77 K. Overall the span of comparative results shows that polyimides are 5 to 10 times more radiation resistant than comparably prepared epoxies. Since gff epoxies are presently less expensive than gff polyimides, it may be prudent to use epoxies at lower dose rate locations. For effective use additional epoxy data between 2 and 20 MGy are needed.

2. The good radiation stability and the generally resilient behavior of Vespel suggest that it might serve as a radiation-resistant gasket material.

3. As interlayer bonds are weakened by irradiation the primary failure mode of laminations changes from tearing of glass-cloth laminae to "delamination," a separation and sliding of adjacent layers. This effect was seen for the flexure and parallel orientation compression tests where there were high interlayer shear stresses. Since the strength of pure polyimide was unchanged for doses studied here, we conclude that the loss in laminate strength is due to deterioration of the glass-to-polyimide adhesion. In the case of Kerimid ⊥ where interlayer shear stresses are small, the failure point probably depends upon how the testing rig allows skewing of the stress direction to develop.

5. In this experiment ^{10}B fission fragment damage accompanied that produced by gamma rays. In terms of energy deposition these two types of radiation were determined to be about equal in the gff materials. In his neutronics calculations for the FED, Engholm [1] finds a corresponding situation at magnet locations where energy deposition by fast neutrons is about equal to that by gamma rays. At this time, however, there are not enough data to determine if energy deposition is a valid criterion for predicting property changes produced by radiations whose damage-producing mechanisms differ greatly. For these two situations, however, ^{10}B fission fragment and fast-neutron damage are far more comparable with each other than either is with gamma-ray damage. From this viewpoint we estimate by comparing the present results with Engholm's calculations that the use of gff polyimide materials as magnet insulators in the FED would make present designs for shields and magnet coils feasible.

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